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WO 02/49980 A1 (54) Title: SUBSTRATES WITH A SELF-CLEANING SURFACE, A PROCESS FOR THEIR PRODUCTION AND THEIR USE

(57) Abstract: Substrates, in particular a substrate of glass, ceramic, plastic and metal and glazed or enamelled substrates, with a self-cleaning surface comprise an at least partly superficially hydrophobic structured (elevations and depressions) coating located on the substrate. Substrates according to the invention comprise particles with an average diameter of less than 100 nm, in particular 5 to less than 50 nm, for formation of the structure of the coating. Compositions according to the invention which are employed for the production of the structured coating of substrates according to the invention comprise, in addition to the structure-forming particles, a layer-forming material in a weight ratio of 100 : 1 to 1 : 2, in particular 20 : 1 to 1 : 1. In addition to having good self-cleaning properties, the coating is distinguished by its transparency. The use of the substrates is aimed in particular at the most diverse glass articles.

**Substrates with a self-cleaning surface, a process for
their production and their use**

Description

5 The invention relates to a substrate with at least one self-cleaning surface, the substrates being in particular a substrate of glass, ceramic, plastic or metal or a glazed or enamelled substrate. The self-cleaning surface located on the substrate is based on a coating with structure-forming particles which is located on the substrate, resulting in a surface structure of elevations and depressions; the surface is at least partly hydrophobic. The invention also relates to a composition for the production of a substrate according to the invention with 10 at least one self-cleaning surface. The invention also relates to a process for the production of the substrate with at least one self-cleaning surface, which comprises coating the substrate with the abovementioned composition. Finally, the invention also relates to the use of the 15 substrates according to the invention with a self-cleaning surface.

It is known that to achieve a good self-cleaning effect on a surface, in addition to a good hydrophobicity this must also have a micro-rough surface structure. Both features 25 are realized in nature, for example in the lotus leaf; the surface form from a hydrophobic material has pyramid-shaped elevations a few μm from one another. Drops of water come into contact substantially only with these peaks, so that the contact area is minuscule, resulting in a very low 30 adhesion. These relationships and the main applicability of the "lotus effect" to technical surfaces are the doctrine of A.A. Abramzon, Khimia i Zhizu (1982), no. 11, 38-40.

Without reference to the lotus effect, US 3, 354,022 discloses water-repellent surfaces, the surface having a micro-rough structure with elevations and depressions and being formed from a hydrophobic material, in particular a 5 fluorine-containing polymer. According to one embodiment, a surface with a self-cleaning effect can be applied to ceramic brick or to glass by coating the substrate with a suspension which comprises glass beads with a diameter in the range from 3 to 12 μm and a fluorocarbon wax based on a 10 fluoroalkyl ethoxymethacrylate polymer. Their low abrasion resistance and moderate self-cleaning effect are a disadvantage of such coatings.

The doctrine of EP 0 909 747 A1 is a process for producing a self-cleaning property of surfaces, in particular roof 15 tiles. The surface has hydrophobic elevations with a height of 5 to 200 μm . Such a surface is produced by application of a dispersion of powder particles of an inert material in a siloxane solution and subsequent curing. As in the process acknowledged above, the structure-forming particles 20 are not fixed on the surface of the substrate in an abrasion-stable manner.

The doctrine of EP Patent 0 772 514 is self-cleaning surfaces of objects with a synthetic surface structure of elevations and depressions, the distance between the 25 elevations being in the range from 5 to 200 μm and the height of the elevations being in the range from 5 to 100 μm and the structure comprising hydrophobic polymers or materials which have been hydrophobized in a stable manner. Etching and embossing processes, and furthermore coating 30 processes are suitable for formation of the structures. If necessary, the formation of the structure is followed by a hydrophobization, for example a so-called silanization.

Similarly structured surfaces with hydrophobic properties are the doctrine of EP 0 933 388 A2. The surface has 35 elevations with an average height of 50 nm to 10 μm and an

average separation of between 50 nm to 10 μm , and a surface energy of the non-structured material of 10 to 20 mN/m. To achieve a particularly low surface energy and thus hydrophobic and oleophobic properties, the structured

5 surface comprises fluorine-containing polymers or has been treated using alkylfluorosilanes. Indications of also using coating processes, instead of the shaping processes disclosed here, for structuring the surface are not to be obtained from this document.

10 The doctrine of DE Patent Application 100 16 485.4 is glass, ceramic and metal substrates with a self-cleaning surface based on a structured and at least partly hydrophobized coating. The coating comprises a glass flux and structure-forming particles with an average particle

15 diameter in the range from 0.1 to 50 μm . The glass flux and structure-forming particles are present in a volume ratio in the range from 0.1 to 5 and the micro-rough surface structure has a ratio of average profile height to average distance between adjacent profile peaks in the range from

20 0.3 to 10. The self-cleaning surface has a higher abrasion resistance than self-cleaning surfaces of roof tiles according to the EP 0 909 747 A1 acknowledged above.

The object of the invention is to provide substrates, in particular substrates of glass, ceramic, plastic and metal

25 and glazed and enamelled substrates, with at least one self-cleaning surface which not only have a low roll-off angle or high contact angle and therefore a good self-cleaning effect, but furthermore are transparent. The self-cleaning surface should have a very high contact angle with

30 respect to water, preferably a contact angle of about/above 150°. The transparency of a transparent substrate, such as glass or plastic, should as far as possible not be reduced. A decoration under the self-cleaning surface should remain clearly detectable. According to a further object, glass,

35 ceramic or metal substrates or glazed or enamelled

substrates according to the invention should have a higher abrasion resistance than substrates which are already known and on which the structured surface is made of an organic polymer or comprises structure-forming particles bonded in 5 an organic polymeric material. According to a further object of the invention, the substrates with the self-cleaning surface according to the invention should be obtainable by means of a simple process, preferably by processes such as are used in the glass and ceramics 10 industry or metal-processing industry for decorating surfaces. These and further objects such as are deduced from the further description do not have to be achieved together in all the embodiments.

The invention accordingly provides a substrate, in 15 particular a substrate of glass, ceramic, plastic and metal or a glazed or enamelled substrate, with at least one self-cleaning surface, comprising a coating which is arranged on the substrate, comprises particles which form a surface structure and is at least partly superficially hydrophobic, 20 which is characterized in that the structure-forming particles have an average diameter of less than 100 nm. The subclaims relate to preferred embodiments.

It has been found that substrates with a superficially hydrophobic coating with a "nanoscale" surface structure 25 have an outstanding self-cleaning effect if the coating comprises structure-forming particles with an average diameter of less than 100 nm. The particle diameter is preferably in the range from less than 50 nm to 5 nm. The term average diameter here is understood as meaning the 30 diameter of primary particles, and not the diameter of agglomerates. In general, at least 90 % and preferably about 100 % of the primary particles have a diameter of less than 100 nm and particularly preferably less than 50 nm. The term "nanoscale" means that the structure has 35 considerably lower profile heights and distances between

profile peaks - apart from in agglomerates these are smaller than the particle diameter - than surfaces with structure-forming particles in the micrometre range.

The structure-forming particles can be organic or inorganic substances. Examples of the inorganic substances which may be mentioned are: metal oxides, mixed oxides, silicates, sulfates, phosphates, borates, metal sulfides, oxosulfides, selenides and sulfoselenides, metal nitrides and oxide-nitrides and metal powders. Examples of the organic structure-forming particles which may be mentioned are carbon blacks and nanoscale organic polymeric particles, and among these fluorine-containing polymers. Many structure-forming particles with the particle diameter according to the claims, such as, in particular, 5 to less than 50 nm, are commercially obtainable. They can otherwise be obtained by precipitation processes which are known per se or by pyrogenic processes, gaseous starting substances being converted into pulverulent substances. The structure-forming particles are particularly preferably metal oxides from the series consisting of silica (SiO_2), titanium dioxide (TiO_2), aluminium oxide (Al_2O_3), zirconium dioxide (ZrO_2) and tin dioxide (SnO_2). These oxides are particularly preferably pyrogenically prepared oxides, and among these in particular silica. Pyrogenic silicas are commercially obtainable with an average primary particle size in the range from about 7 to 40 nm.

In addition to the structure-forming particles, the self-cleaning surface of substrates according to the invention comprises a layer-forming material, which can be an inorganic or organic material. The layer-forming material either forms a homogeneous layer in which the structure-forming particles are fixed in the form of their primary particles and/or agglomerates, or the structure-forming particles are fixed on the substrate by means of the layer-forming material. Some of the primary particles and/or

agglomerates thereof project at least partly out of the surface and in this manner form elevations and depressions, which, in addition to the hydrophobization, are responsible for the effect according to the invention.

5 Among the layer-forming materials, inorganic materials are particularly preferred. The material is expediently a vitreous material. Such a material can have been formed in the context of ceramic firing from one or more glass frits or glass-forming raw materials. During the firing, the

10 vitreous material encloses structure-forming particles such that some of these project out of the surface. The glass frits employed for the production of the self-cleaning surface according to the invention are those with a composition which has a melting point below that of the

15 structure-forming particles and below the deformation temperature of the substrate to be coated.

According to an alternative embodiment, the vitreous material is a substance which, during firing from one or more glass-forming raw materials, in particular low-melting

20 oxidic or sufficiently reactive raw materials, forms vitreous bonds with constituents of the substrate and/or some of the structure-forming particles. These bonds are structural elements of the general formula $Me-O-Me'$, wherein Me and Me' can be identical or different and

25 represent boron, silicon, phosphorus, aluminium, titanium, tin, zirconium or other metals of the substrate.

An example of a material which contains $Me-O-Me'$ structural elements and in which the structure-forming particles are embedded is a system such as is obtained, during firing

30 carried out after coating, by coating glass or a vitreous or enamelled substrate with a composition comprising boric acid and/or an alkali metal phosphate and structure-forming particles. The boric acid and/or the phosphate thus form a chemical bond to reactive groups of the glass substrate or

the glazing/enamel layer and optionally additionally the structure-forming particles during the firing.

According to a further alternative, coating materials with Me-O-Me' structural elements are those systems such as are

5 formed from organometallic compounds of the elements boron, silicon, aluminium, titanium and zirconium which have at least two hydrolysable groupings during alcoholysis/hydrolysis with a subsequent condensation reaction and optionally subsequent firing.

10 According to a preferred embodiment of the substrate according to the invention with a self-cleaning surface, the structured coating comprises structure-forming particles with an average diameter of less than 100 nm, in particular in the range from 5 nm to less than 50 nm, and a

15 layer-forming inorganic or organic material in a weight ratio in the range from 100 : 1 to 1 : 2, in particular 20 : 1 to 1 : 1. A ratio outside the limits mentioned is indeed possible, but if the content of layer-forming material is too low, a possibly inadequate fixing of the

20 structure-forming particles is the consequence. In the case of too high a content of the layer-forming material, the self-cleaning effect decreases because the structure-forming particles may be sunk too low in the layer-forming material.

25 Preferred substrates have a coating which substantially comprises structure-forming particles and a layer-forming inorganic material, but the coating can additionally comprise adhesion promoters or those compounds such as are formed from auxiliary substances present and/or precursors

30 of the layer-forming material during the production of the coating, including a heat treatment step which may be necessary or firing.

In order to impart to the structured surface the necessary hydrophobic properties and also the desired high contact

angle, in particular about/above 150°, or low roll-off angle, in particular about/below 1°, there is on the structured layer as a rule a hydrophobic layer, for example one such as is obtained by silanization.

- 5 According to a further embodiment, the self-cleaning surface according to the invention also comprises, in addition to the nanoscale elevations and depressions produced by the structure-forming particles, an over-structure, elevations and depressions in regular or
- 10 stochastic distribution forming a micro-rough structure. The term "micro-rough" means a height of the profile peaks and a distance between the profile peaks in the range from 0.1 to 50 µm, in particular 0.5 to 15 µm. Such substrates according to the invention with a nanoscale and
- 15 additionally a microscale surface roughness can have a single or two structure-forming coatings on the substrate, in the first case the nanoscale and microscale particles being distributed in a layer-forming material. In the second case there is a coating with the nanoscale particles
- 20 on a coating with the microscale particles which has been applied beforehand.

According to a particularly preferred embodiment, the substrate is a glass or an enamelled glass, the coating according to the invention to achieve the self-cleaning properties being substantially transparent.

Substrates according to the invention with a self-cleaning surface have a superficially hydrophobic coating. If the coating itself does not have hydrophobic properties, this property is effected by application of a substance having a hydrophobizing action to the structured surface.

30 Organosilanes, and here in particular fluorine-containing organosilanes, are particularly expedient for the hydrophobization. If the coating material of the structure-forming surface is a vitreous material, Si-O-Si structural elements can also be formed by using organosilanes having a

hydrophobizing action, as a result of which the component having a hydrophobizing action is fixed firmly to the structured substrate and the self-cleaning properties thus remains [sic] permanently.

5 The invention furthermore relates to the process for the production of substrates according to the invention and to compositions such as are used in the production thereof.

The compositions for the production of a substrate according to the invention with a self-cleaning surface are

10 substance mixtures which comprise structure-forming particles with an average particle diameter of less than 100 nm, in particular particles with an average particle diameter in the range from 5 nm to less than 50 nm, and a layer-forming particulate or liquid material. As mentioned
15 above, the particle diameter is that of the primary particles and the diameter of at least 90 %, preferably substantially of all the particles, is preferably less than 100 nm, or less than 50 nm.

20 The layer-forming particulate or liquid material can be an organic or inorganic material. The term "layer-forming material" is understood as meaning a material which, in the context of application to the substrate by a physical or chemical route, is capable of forming a homogeneous layer and of fixing the structure-forming particles in the layer
25 or/and on the substrate. If the material is an organic polymeric material or precursors of a polymer, this is present in the composition in the form of a solution in an organic or aqueous solvent or solvent mixture or in the form of an organic or aqueous suspension. The homogeneous
30 layer is achieved by evaporation of the solvent and/or during a subsequent heat treatment by fusing together thermoplastic particles or by a condensation or polyaddition or polycondensation.

According to preferred embodiments of the composition, this comprises inorganic layer-forming materials or at least precursors thereof. Particularly suitable layer-forming organic materials are glass frits and oxidic raw materials (= precursors) which are capable of glass formation with other substances, such as, in particular, boric acid (B_2O_3), bismuth oxide (Bi_2O_3), alkali metal and alkaline earth metal oxides, zinc oxide and lead oxide as well as alkali metal silicates, and phosphates and borates. Most glass-forming substances are contained in the composition in particulate form. Alkali metal oxides and alkali metal silicates are expediently contained in the composition in the form of aqueous alkali solution or in the form of water-glass (sodium silicate solution).

According to a further alternative, the compositions according to the invention comprise an organometallic compound of one or more of the elements boron, silicon, aluminium, titanium and zirconium as the layer-forming material. The organometallic compounds are preferably those which contain alkoxy groups, acetyl groups or acetylacetone groupings, so that $Me-O-Me'$ structural elements are formed by a condensation reaction, wherein Me and Me' can be identical or different and represent the elements mentioned.

The structure-forming particles and the layer-forming material are usually contained in the composition according to the invention in a weight ratio of 100 : 1 to 1 : 2; the weight ratio is preferably in the range from 20 : 1 to 1 : 1.

Pulverulent compositions according to the invention can be applied to the substrate by dusting or by electrostatic coating.

A preferred embodiment of the composition according to the invention also comprises, in addition to the layer-forming

materials and the structure-forming particles, a liquid medium. The consistency of such a composition can be in wide ranges, for example for the purpose of application by spraying or dipping, a considerably lower viscosity is

5 established than in the case of application of the composition by a conventional printing process. In the case of use of the composition by a printing process, for example a screen printing process, the consistency of the composition is preferably paste-like.

10 Particularly preferred compositions which are suitable for the formation of a structured surface of a substrate of glass, ceramic, metal or a glazed or enamelled substrate comprise, as the layer-forming material, one or more glass frits as the main component, the softening point of these

15 being sufficiently below the deformation temperature of the substrate to be coated. If the composition comprises raw materials which are capable of glass formation (= precursors), those substances which are capable of undergoing chemical bonding with one another and/or with

20 structural elements of the substrate and/or structural elements of the nanoscale particles under conventional firing conditions are chosen. Boric acid and alkali metal phosphates are particularly suitable layer-forming materials or precursors thereof.

25 Using a liquid to paste-like composition which comprises boric acid or an alkali metal dihydrogen phosphate as the layer-forming material or precursor thereof and a pyrogenic oxide as the structure-forming material, a firmly adhering structured surface can be formed on glass which, after

30 hydrophobization with an organosilane, in particular a fluorine-containing organosilane, leads to particularly good self-cleaning properties. The contact angle of a glass coated in this way is above 150°.

The liquid medium can be an organic or organic-aqueous or

35 aqueous medium, which can comprise processing auxiliaries,

such as agents to adjust the viscosity, in addition to the obligatory components.

The surface of the micro-rough layer is at least partly hydrophobized, in particular the peaks and elevations.

- 5 Preferably, however, the entire surface is hydrophobized. The hydrophobization substantially comprises a very thin coating, for example of a thickness of 1 to 10 nm, which adheres firmly to the underlying surface. This adhesion is effected by film formation of the coating composition after 10 application. Preferred hydrophobizing agents are bonded chemically to the substrate, for example via an Si-O-Si bridge. Such bridges result from the reaction of a silanol group of a silicatic material of the structured coating with an alkoxy silane or alkoxy siloxane. Preferred 15 substrates according to the invention with a self-cleaning surface have a coating, often only a few atom layers thick, based on an alkyltrialkoxy silane and preferably a longer-chain fluoroalkyltrialkoxy silane or oligomers of these silanes.
- 20 The substrates according to the invention with a self-cleaning surface can be produced in a simple manner by a process which comprises the following steps:
 1. coating of a surface of the substrate with a composition comprising structure-forming particles and an inorganic or 25 organic layer-forming material, this composition being pulverulent or, preferably, liquid to paste-like,
 2. formation of a cohesive layer which fixes the structure-forming particles and adheres firmly to the substrate and
 3. hydrophobization of the structured surface with a 30 hydrophobizing agent, in particular an organosilane, which adheres firmly to the structured surface or forms a chemical compound with this.
- 35 A particular feature of the process is the use of structure-forming particles with an average diameter of less than 100 nm, preferably less than 50 nm, and at least

5 nm. The profile heights of the elevations are, if no particles in the μm range which form an over-structure are present, less than 100 nm, in particular less than 50 nm. The structure-forming particles and the layer-forming 5 materials are those which have already been mentioned above.

The compositions to be applied by means of a conventional coating process preferably comprise the constituents essential to the invention, that is to say the structure-forming particles and the layer-forming material, in a 10 ratio of amounts which has already been mentioned above. If a pulverulent composition is used for the coating, this can be carried out by dusting the substrate or by electrostatic coating. The coating is preferably carried out using a 15 liquid to paste-like composition, the liquid media contained in such a composition being those systems such as are known to the expert, in particular the decoration expert in the glass and ceramics industry. The coating with a liquid to paste-like composition can be carried out by 20 spraying, brushing, pouring or dipping or by means of a conventional printing process, such as a screen printing or a dabber transfer printing process.

The feature "formation of a cohesive layer which adheres firmly to the substrate and fixes the structure-forming 25 particles" can vary according to the substrate to be coated and the composition of the coating composition. If the composition comprises an organic polymeric material which is pulverulent or suspended in a liquid medium, a cohesive layer can be produced by passing the coated substrate to a 30 heat treatment, solvent optionally present evaporating and polymer particles fusing together or, in the case of multi-component systems, reacting to give a polymeric material.

Compositions which are applied to a substrate which can undergo firing, that is to say a glass, ceramic or metal 35 substrate or a glazed or enamelled substrate, and comprise

a glass frit or constituents which are capable of glass formation with the substrate surface and/or the particles, can be converted into a cohesive structured layer by a heat treatment, that is to say in this case firing. During

5 firing, the glass frit melts to a homogeneous layer; the constituents of the composition which are capable of glass formation form [sic] a chemical reaction with reactive groups of the substrate and/or the structure-forming particles to form vitreous structures with structural

10 elements of the formula $Me-O-Me'$, wherein Me and Me' have the meaning already given. The glass frits and/or constituents capable of glass formation contained in the composition are chosen such that the heat treatment, that is to say the firing, can be carried out at a temperature

15 below the deformation temperature of the substrate. In the coating of glass, the composition will accordingly comprise those layer-forming constituents which melt below 650 °C, in particular in the range from 450 to 600 °C and can form the required structures.

20 The nanostructured coating to be applied to the substrate can have a varying layer thickness. Preferably, the layer thickness of layers which comprise as structure-forming particles exclusively particles according to the invention with an average diameter of less than 100 nm, in particular

25 less than 50 nm, and at least 5 nm is in the range from 5 to 1000 nm. If the composition additionally comprises larger structure-forming particles, for example particles with a diameter in the range from 0.5 to 15 μm , the maximum height of the layer is of course higher. In the case

30 mentioned last, the nanoscale structure according to the invention is on a micro-rough over-structure. Alternatively, it is also possible for a substrate with a micro-rough surface structure, for example a surface structure such as substrates according to DE Patent

35 Application 100 16 485.4 have, already to be coated with a composition according to the invention which comprises as

structure-forming particles substantially only particles with a particle diameter of less than 100 nm, preferably less than 50 nm, to be baked and then to be hydrophobized.

After the formation of the structured surface, the 5 hydrophobization stage follows:

The hydrophobization can be carried out by application of a hydrophobic lacquer or by polymerization of monomers on the micro-rough surface. Suitable polymeric lacquers are solutions or dispersions of e.g. polyvinylidene fluoride. A 10 hydrophobization can also be carried out by plasma polymerization of completely or partly fluorinated vinyl compounds.

The hydrophobization is particularly expediently carried out using reactive alkyl- or, preferably, 15 fluoroalkylsilanes and oligomeric alkyl- or fluoroalkylsiloxanes. The silanes or siloxanes preferably contain one or more alkoxy or acetyl groups, such as ethoxy groups, as the reactive group. Crosslinking of the hydrophobizing agent and also chemical bonding thereof to a 20 silicatic surface containing silanol groups is possible by means of these functional groups. Silanizing agents which are particularly preferably to be used are tridecafluoroctyltriethoxysilane and oligomers thereof. Such products can be applied to the surface to be 25 hydrophobized in the form of dilute organic, in particular alcoholic, aqueous-organic and aqueous solutions, for example by dipping, spraying or brushing.

After application of a solution comprising a fluorine-containing silane or siloxane to the substrate, the 30 substrate is dried and cured, preferably at a temperature of up to 500 °C, for example for 30-60 min at about 150 °C, 10-15 min at 250 to 300 °C or 1 min at about 500 °C. The optimum of the after-treatment with heat in respect of

highest abrasion resistance is at a temperature in the range from 200 to 300 °C.

Using dilute solutions of the silanes or siloxanes mentioned, layers a few nm thick which have a very high 5 chemical and mechanical resistance and are 2- and 3-dimensional siloxane networks are obtained.

The hydrophobic layers accessible using reactive fluoroalkylsilanes or -siloxanes are distinguished by a similarly good hydrophobicity and oleophobicity, so that 10 substrates according to the invention contaminated with hydrophobic dirt particles can also easily be cleaned with water.

The invention also relates to the use of a substrate according to the invention with a self-cleaning surface. 15 Examples are glass panes for vehicles and windows, construction glass, ceramic tiles, roof tiles, covers on photovoltaic solar cells, metal profiles and lacquered substrates, such as car lacquers.

The substrates according to the invention with a self-cleaning surface are distinguished by a very high 20 efficiency of the self-cleaning property. The contact angle of preferred substrates according to the invention with respect to water is in general about and often above 150°.

A particularly outstanding feature of substrates according 25 to the invention is the transparency of the nanostructured coating. Transparent substrates of plastic and glass and glazed or enamelled substrates are accordingly particularly suitable for being provided with a transparent coating according to the invention and therefore for obtaining 30 high-quality self-cleaning surfaces which are themselves transparent and therefore also clearly reveal underlying decorations.

Essential advantages of compositions according to the invention are their easy accessibility and range of variation in respect of composition. The compositions can therefore be used for coating the most diverse substrates 5 and producing good self-cleaning properties.

The stages of the process according to the invention are based closely on those process stages such as are used, for example, for decoration purposes in the glass and ceramics industry, but are also conventional in the lacquering of 10 metallic substrates with stoving lacquers. The devices and technologies known to the expert can therefore be used.

Examples

Production of float glass or high-grade steel with a transparent self-cleaning surface

15 1. 4 mm float glass was coated with a composition according to the invention by means of screen printing. The composition comprised 0.5 wt.% boric acid (B_2O_3) and 4 wt.% pyrogenic silica in a screen printing medium (no. 80858 from dmc² AG). The pyrogenic silica had an 20 average diameter of the primary particles of 12 nm. The printing medium was a water-friendly medium. The screen printing was carried out using a 100 T screen. After drying, the coating was shock-fired at 660°C in the course of 4 min. The hydrophobization of the structured 25 stoved surface was carried out using a fluoroalkylsilane formulation, that is to say an ethanolic solution of tridecafluoroctyltriethoxysilane. The solution was introduced over the surface, and curing was then carried out at elevated temperature.

30 The float glass coated in this way was transparent and had a contact angle of above 150°.

2. Example 1 was repeated with the only difference that the composition comprised 0.5 wt.% diammonium hydrogen phosphate ((NH)₂HPO₄) [sic] instead of boric acid as the layer-forming material. After the hydrophobization, the 5 glass coating showed outstanding self-cleaning properties.

It is assumed that during firing vitreous structures with the structural element Si-O-B or Si-O-P or metal-O-P form between the boric acid or the phosphate and reactive centres of the glass or metal and the structure-forming silica particles.

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3. Substrate was degreased V4A high-grade steel. A composition with 4 wt.% pyrogenic silica (d = 12 nm) and diammonium hydrogen phosphate in an amount of (a) 0.25 wt.%, (b) 0.5 wt.% and (c) 1.0 wt.% in screen printing medium 80858 was used for the coating. After coating by means of screen printing, firing was carried out for 6 minutes at 660 °C. A scratch-resistant self-cleaning surface was obtained in all three cases.

Patent claims

1. Substrate, in particular a substrate of glass, ceramic, plastic and metal or a glazed or enamelled substrate, with at least one self-cleaning surface, comprising a coating which is arranged on the substrate, comprises particles which form a surface structure and is at least partly superficially hydrophobic, characterized in that the structure-forming particles have an average 10 diameter of less than 100 nm.
2. Substrate with a self-cleaning surface according to claim 1, characterized in that the structure-forming particles have an average 15 diameter of less than 50 nm and at least 5 nm.
3. Substrate with a self-cleaning surface according to claim 1 and 2, characterized in that the structure-forming particles are chosen from the 20 series consisting of metal oxides, mixed oxides, silicates, sulfates, phosphates, borates, carbon blacks, metal powders, metal sulfides, selenides, sulfoselenides and oxosulfides, metal nitrides and oxide-nitrides and organic polymers.
- 25 4. Substrate with a self-cleaning surface according to one of claims 1 to 3, characterized in that the structure-forming particles are metal oxides from the series consisting of SiO_2 , TiO_2 , Al_2O_3 , ZrO_2 and 30 SnO_2 , in particular pyrogenically prepared oxides thereof.
5. Substrate with a self-cleaning surface according to one of claims 1 to 4,

characterized in that
the coating comprises the structure-forming particles
bonded in or by means of an inorganic or organic layer-
forming material.

5 6. Substrate with a self-cleaning surface according to
claim 5,
characterized in that
the layer-forming material is a glass or a material
which forms Me-O-Me' structural elements, wherein Me
10 and Me' are identical or different and represent B, Si,
Al, P, Ti, Sn or Zr.

7. Substrate with a self-cleaning surface according to one
of claims 1 to 6,
characterized in that
15 in addition to the structure-forming particles
according to the invention with an average diameter of
less than 100 nm, in particular less than 50 nm, the
layer according to the invention or a layer applied
underneath with a micro-scale surface structure also
20 comprises particles which form an over-structure and
have an average diameter of 0.1 to 50 μm , in particular
0.5 to 15 μm .

8. Substrate with a self-cleaning surface according to one
of claims 1 to 7,
25 characterized in that
the coating comprises structure-forming particles with
an average diameter of less than 100 nm, in particular
less than 50 nm, and one or more layer-forming
inorganic or organic materials in a weight ratio in the
30 range from 100 : 1 to 1 : 2, in particular 20 : 1 to
1 : 1.

9. Substrate with a self-cleaning surface according to one
of claims 1 to 8,
characterized in that

the substrate is glass or a plastic or an enamelled or glazed substrate.

10. Substrate according to claim 9,
characterized in that

5 the substrate is glass and the substrate coated
according to the invention is substantially
transparent.

11. Composition for the production of a substrate with at
least one self-cleaning surface according to one of
10 claims 1 to 10,

characterized in that
it comprises structure-forming particles with a
particle diameter of less than 100 nm, in particular
less than 50 nm, and at least 5 nm, and a layer-forming
15 particulate or liquid material in a weight ratio of
100 : 1 to 1 : 2.

12. Composition according to claim 11,
characterized in that

20 the layer-forming material comprises as the main
component one or more glass frits or/and one or more
glass raw materials which, during firing, form a glass
or vitreous structures with one another or/and with
groups of the substrate or/and of the structure-forming
particles which are capable of glass formation.

25 13. Composition according to claim 12,
characterized in that

it substantially comprises structure-forming particles
and a layer-forming, in particular particulate
material, which can be suspended in a liquid medium.

30 14. Composition according to one of claims 11 to 13,
characterized in that

it comprises structure-forming particles according to
the invention with a particle diameter of less than

50 nm and at least 5 nm, in particular a silica, and, as the layer-forming material, one or more oxides from the series consisting of B_2O_3 , Bi_2O_3 , alkali metal oxides, zinc oxides and lead oxides or borates, 5 silicates or phosphates or a glass frit which melts below 650 °C.

15. Composition according to claim 14, characterized in that it substantially comprises 1 to 10 wt.% pyrogenic 10 silica (SiO_2) and 0.1 to 2 wt.% boric acid (B_2O_3), alkali metal or ammonium dihydrogen phosphate or di-alkali metal or diammonium hydrogen phosphate or a glass frit which melts below 600 °C, in each case based on the composition, and a printing medium.

15 16. Process for the production of a substrate with at least one self-cleaning surface according to claims 1 to 10, comprising (i) coating of a surface of the substrate with a composition comprising structure-forming particles and an inorganic or organic layer-forming 20 material, (ii) formation of a cohesive layer which fixes the structure-forming particles and adheres firmly to the substrate and (iii) hydrophobization of the structured surface formed, characterized in that 25 the structure-forming particles have an average diameter of less than 10 nm, preferably less than 50 nm, and at least 5 nm.

17. Process also [sic] claim 16, characterized in that 30 a substrate from the series consisting of glass, ceramic, plastic and metal and glazed or enamelled substrates which can already have a micro-rough surface is coated with a composition according to one of claims 11 to 15 which comprises a glass frit or a glass-forming raw material, the coated substrate is subjected 35

to firing suitable for the formation of a firmly adhering cohesive layer, and the structured surface contained [sic] is coated with an organosilane, in particular fluoroorganosilane, and thereby hydrophobized.

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18. Process according to claim 16 or 17, characterized in that the composition used to form the surface structure is applied in a liquid to paste-like consistency by means of a printing process, by spraying, brushing, pouring or dipping.

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19. Use of a substrate with a self-cleaning surface according to one of claims 1 to 10 or obtainable by a process according to one of claims 16 to 18 for the production of glass panes for vehicles and windows, construction glass, ceramic tiles, roof tiles, covers on photovoltaic solar cells, metal profiles and lacquered substrates.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/14168

A. CLASSIFICATION OF SUBJECT MATTER	IPC 7 C03C17/42	C04B41/52	C23C24/08	C23C24/10	C23C30/00
	C03C8/14	C03C8/20	C03C17/34		

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C03B C04B C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, COMPENDEX, FSTA, INSPEC, IBM-TDB

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 658 525 A (NISSAN MOTOR ;CENTRAL GLASS CO LTD (JP)) 21 June 1995 (1995-06-21) examples 4-15 page 11, line 22 -page 13, line 5 ---	1-13,16, 18,19
Y	EP 0 748 775 A (CENTRAL GLASS CO LTD) 18 December 1996 (1996-12-18) examples	14,15
X	EP 1 075 867 A (TOTO LTD) 14 February 2001 (2001-02-14)	1-13,16, 18,19
Y	& WO 99 51327 A (TOTO) 14 October 1999 (1999-10-14) ---	14,15
P,Y	EP 0 684 075 A (TOTO LTD) 29 November 1995 (1995-11-29) examples 1-35 ---	14,15
Y	EP 0 684 075 A (TOTO LTD) 29 November 1995 (1995-11-29) examples 1-35 ---	14,15
	-/-	

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

- *&* document member of the same patent family

Date of the actual completion of the international search

29 May 2002

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/14168

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	WO 01 74739 A (DMC 2 DEGUSSA METALS CATALYTS ;FRITSCHE KLAUS DIETER (DE); POTH LU) 11 October 2001 (2001-10-11) cited in the application the whole document -----	1-16, 18, 19

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 17

"SIC!" RENDERS THE CLAIM TOTALLY OBSCURE... IT IS NOT EVEN CLEAR WHETHER THIS CLAIM IS A DEPENDENT OR AN INDEPENDENT CLAIM.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No
PCT/EP 01/14168

Patent document cited in search report	Publication date		Patent family member(s)	Publication date
EP 0658525	A 21-06-1995		JP 7138050 A JP 7267684 A DE 69422964 D1 DE 69422964 T2 DE 69430396 D1 EP 0658525 A2 EP 0866037 A2 US 5674625 A US 5856016 A	30-05-1995 17-10-1995 16-03-2000 15-06-2000 16-05-2002 21-06-1995 23-09-1998 07-10-1997 05-01-1999
EP 0748775	A 18-12-1996		JP 3183806 B2 JP 8325036 A JP 9132433 A EP 0748775 A2	09-07-2001 10-12-1996 20-05-1997 18-12-1996
EP 1075867	A 14-02-2001		AU 9095898 A EP 1075867 A1 CN 1295493 T WO 9951327 A1	25-10-1999 14-02-2001 16-05-2001 14-10-1999
EP 0684075	A 29-11-1995		JP 7155598 A JP 7191011 A JP 7232080 A JP 8103488 A JP 3225761 B2 JP 8108075 A JP 3246235 B2 JP 8117606 A JP 8131524 A JP 8131834 A JP 8131842 A AU 1199895 A EP 0684075 A1 US 5853866 A CA 2155822 A1 CN 1120819 A WO 9515816 A1 TW 406031 B US 6268050 B1 US 6027797 A US 6294246 B1 US 6210779 B1 US 6294247 B1 JP 8066635 A JP 3261909 B2 JP 7222928 A JP 8150197 A AU 678330 B2 AU 1199595 A JP 8224481 A	20-06-1995 28-07-1995 05-09-1995 23-04-1996 05-11-2001 30-04-1996 15-01-2002 14-05-1996 28-05-1996 28-05-1996 28-05-1996 27-06-1995 29-11-1995 29-12-1998 15-06-1995 17-04-1996 15-06-1995 21-09-2000 31-07-2001 22-02-2000 25-09-2001 03-04-2001 25-09-2001 12-03-1996 04-03-2002 22-08-1995 11-06-1996 22-05-1997 27-06-1995 03-09-1996
WO 0174739	A 11-10-2001		DE 10016485 A1 WO 0174739 A1	11-10-2001 11-10-2001